METHODS FOR THE PRODUCTION OF ~~MARBLE-LIKE~~ CRYSTALLIZED GLASS PANEL WITH EMBOSSED SURFACE

~~CROSS REFERENCE TO RELATED APPLICATIONS~~

~~[0001] U.S. Pat. No. 3,554,725 January/1971 Bracken et al.~~

~~[0002] G.B.142779201/1972 Nippon Electric Glass~~

~~[0003] U.S. Pat. No. 3,672,859 June/1972 Claussen~~

~~[0004] U.S. Pat. No. 3,843,343 October/1974 Okada et al.~~

~~[0005] U.S. Pat. No. 3,955,989 May/1976 Nakamura~~

~~[0006] U.S. Pat. No. 4,054,435 October/1977 Sakane et al.~~

~~[0007] U.S. Pat. No. 4,746,347 May/1988 Sensi~~

~~[0008] U.S. Pat. No. 5,089,345 February/1992 Hashibe et al.~~

~~[0009] U.S. Pat. No. 5,403,664 April/1995 Kurahashi et al.~~

~~[0010] U.S. Pat. No. 5,885,315 March/1999 Fredholm et al.~~

~~BACKGROUND~~ FIELD OF INVENTION

[0011] This invention relates to the process of producing flat crystallized glass panel with embossed surface which results stereoscopic aspect and better static friction on the surface to prevent from slipping under wet condition, so it can better be used on floor application and others.

BACKGROUND OF THE INVENTION

[0021] The crystallized glass is an ideal substitution of natural stone as ornamental building materials because of its superior mechanical strength, heat resistance, and efflorescence resistance. ~~In general, all flat or curved~~ Conventional crystallized glass articles have glossy and smooth surface, and therefore have very limited application on floor due to the potential risk of slip.

[0022] Manufacture of crystallized glass articles begins with production of a crystallizable glass composition ~~Crystallizable glass can be obtained~~ by heating the special formulated, mixed raw materials of glass at a temperature of over 1400° ~~.degree.~~ C. ~~The molten glass is water granulated into glass granules. During the crystallizing process, glass granules are softened, deformed, and fusion-bonded together along their interfaces. Along with the desired temperature profile, the .beta.-type needle-like crystals are formed from the surface of the glass granules toward the interior (crystallization).~~ Granules of crystallizable glass are typically packed into a mold for crystallization. Upon [[In]] completion of the crystallization, the integral crystallized glass article is obtained ~~(G.B. 1427792, 1972; U.S. Pat. No. 3,843,343, 1974, Okada et al.; U.S. Pat. No. 3,955,989, 1976, Nakamura; U.S. Pat. No. 4,054,435, 1977, Sakane et al.; U.S. Pat. No. 5,403,664, 1995, Kurahashi et al.).~~

[0023] The ~~present invention relates to a process of producing crystallized glass, requires no special molds, consists of~~ six general steps of manufacturing crystallized glass articles are:

[0024] (1) ~~Molten glass materials:~~ Crystallizable glass is formulated such as from [[of]] the systems ~~SiO.sub.2--Al.sub.2O.sub.3--CaO or SiO.sub.2--Al.sub.2O.sub.3--CaO--ZnO,~~ SiO_2-Al_2O_3-CaO, SiO_2-Al_2O_3-CaO-ZnO, or others may be employed. The formulated glass materials are heated at ~~1400-1600.degree.~~ 1400 to 1600° C. to melt them together.

[0025] (2) Water granulation: The molten ~~glass (1)~~ crystallizable glass of step 1 is granulated in water into glass particles with less than 10 mm in size. The ideal water temperature is around ~~40-60.degree.~~ 40 to 60° C. The ~~granulated~~ crystallizable glass ~~particles~~ granules are collected and dried.

[0026] (3) Molding: The ~~granulated~~ crystallizable glass ~~particles~~ granules are ~~loaded on~~ packed into a flat refractory mold with surrounding frames. The ~~top surface~~ floor of the mold and interior surfaces of the frames are coated with a mold release agent ~~(Al.sub.2O.sub.3 powder or others)~~. such as alumina powder.

[0027] (4) Crystallizing: ~~During heat-treated process,~~ The loaded mold is heat treated using a specified temperature profile, such that the glass granules are softened, deformed and fusion-bonded together along their interfaces. ~~Along with the desired temperature profile, the .beta.-type n~~ Needle-like crystals are formed from the surface of the glass granules toward the interior (crystallization).Conventionally, the loaded mold is heated at a constant rate and may be held at a high temperature for as much as one to two hours. In completion of the crystallizing process, the integral crystallized glass article is obtained.

~~[0028] (5) Flow deformation: At liquefied temperature, the flow deformation is formed and advanced on the surface of glass article to fill up the space among glass particles to produce a smooth and even surface .~~

[0029] ([[6]] 5) Cooling: A proper temperature profile is applied for cooling, so the glass article will not crack or distort.

DISCUSSION OF PRIOR ART

[0012] Crystallized glass has been utilized in the manufacturing of such varied articles as

cookware, tableware, missile nose cones, protective shields, and in the computer and electronics field. Nowadays, crystallized glass has been used as ornamental building materials to replace the natural stones due to its excellent characteristics in mechanical strength, heat-resistance, chemical corrosion strength, and water resistance, and has obtained great popularity. However, its glossy and smooth surface together with its pure color often creates simple and cold environmental feelings. Several patents (G.B. 1427792, 1972; U.S. Pat. No. 3,843,343, 1974, Okada et al.; U.S. Pat. No. 3,955,989, 1976, Nakamura; U.S. Pat. No. 5,403,664, 1995, Kurahashi et al.) disclose the methods of producing surface pattern over crystallized glass flat panel. However, these methods are limited in changing the color pattern of the surface rather than the roughness of the surface. As a result, the crystallized glass has inherited the smooth and glossy characteristic of glass and has limited its use from floor application due to the potential risk of slip.

[0013] The U.S. Pat. No. 5,089,345, 1992, Hashibe et al. states that it is uneconomical to apply molds with rough and uneven surface to produce crystallized glass with uneven surface, and discloses a method of producing crystallized glass with an irregular rough surface pattern. However, the rough surface is produced by overlapping flaky and flattened crystallized pieces at "random" at the bottom of the glass article. The resulted surface is therefore unpredictable.

[0014] Many U.S. Patents (U.S. Pat. No. 3,554,725, 1971, Bracken et al.; U.S. Pat. No. 3,672,859, 1972, Classen; U.S. Pat. No. 4,746,347, 1988, Sensi; U.S. Pat. No. 5,885,315, 1999, Fredholm et al.) disclose methods of using molten glass to form glass sheets with rough surface patterns through mechanical rollers. However, the process is not adequate for producing ~~marble-like~~ crystallized glass suitable for use in flooring.

Crystallized glass, also known as glass ceramic, could be a desirable material for flooring. Glass ceramic is beautiful and durable.

Floors of polished stone or conventional glass ceramic have two disadvantages. The reflective surface can be unattractive or painful to the eyes under certain lighting. The surface is slick and can be dangerous to walk on, especially if any oil or moisture are present.

There is thus a need for glass ceramic flooring that does not reflect light in a mirror-like manner. There is further a need for glass ceramic flooring that has a higher coefficient of friction than polished stone or conventional glass ceramic, so that the flooring is safe to walk on even when wet.

~~OBJECTS AND ADVANTAGES~~

~~[0015] The main objective of the present invention relates to marble-like crystallized glass articles is to provide methods to produce a regular or irregular embossed surface.~~

~~[0016] The present invention that produces crystallized glass with regular or irregular embossed surfaces can increase the static friction of its surface over 20%, comparing to the traditional smooth surface, to better prevent from slipping under wet conditions.~~

~~1~~

~~[0017] The present invention that produces crystallized glass with regular or irregular embossed surface can create a stereoscopic aspect with less mirror-like light reflection to provide better visual comfort.~~

~~[0018] The present invention that produces crystallized glass with regular or irregular embossed surface has uniform, predictable and consistent surface pattern.~~

~~[0019] The present invention requires no additional tools. It is accomplished by controlling the crystallizing temperature profile and the Molding procedures over various sizes of glass particles.~~

~~[0020] The present invention is cost effective and economically ideal for mass~~

~~production.~~

SUMMARY OF INVENTION

[0030] ~~The original crystallized glass articles and natural stone, such as marble or granite, have a polished, smooth, and glossy surface. The present invention is to produce the crystallized glass with embossed surface. It creates a stereoscopic aspect over the surface for better visual comfort and increases static friction to prevent from slipping under wet conditions. The invention requires no additional tools but various process techniques. It is cost effective and easy to be adopted for mass production.~~

~~[0031] It is possible to produce a rough surface of the glass articles by overlapping crystallizable glass pieces at the bottom of the mold and uses it as principal surface (ref U.S. Pat. No. 5,089,345). However, the surface condition is hard to predict and is not adequate for mass production.~~

[0032] The present invention provides two ~~different~~ related methods in producing crystallized glass plates with an embossed ~~or un-even~~ , that is, textured, surface. Both methods result in a textured top surface of the glass ceramic plate after the flow deformation this sense step. The texturing of the finished plate is ornamental; but more importantly, it greatly reduces glare and slipperiness of the plate, even when wet. Crystallized glass plates produced by the methods of the present invention have a coefficient of friction that is at least 20% greater than that of crystallized glass plates produced by conventional methods. The methods of the present invention require no special equipment or molds and are easily adapted for mass production of glass ceramic articles of consistent quality.

[0033] Method 1~~: to control the flow deformation process to obtain the embossed surface (FIGS. 1a-1c).~~ relies solely on careful control of the temperature profile during the flow deformation step to produce a glass ceramic plate with a suitably textured top surface that is free of pinholes. After polishing, the finished plate has a surface that is textured by a

network of unpolished craters that are about 0.2 to 0.5 mm deep.

[0034] Method 2 ~~: to load the glass particles with both glass bits and pieces to create the variation of the density of the glass body, so as to produce an uneven surface (FIG. 2a 2f).~~ further includes loading the mold with flat pieces of crystallized glass underneath the granules of crystallizable glass. The finished plate has a surface that is textured by raised areas above the flat pieces of precrystallized glass. The raised areas are typically about half as high as the original thickness of the precrystallized glass.

BRIEF DESCRIPTION OF DRAWINGS

[0035] FIG 1a illustrates that the glass body is prepared by loading various sizes of glass particles into the mold and ready for crystallization process.

[0036] FIG 1b (Prior Art) illustrates ~~that the flow deformation smoothes the surface.~~ a smooth top surface created by the flow deformation process if the crystallizing step is performed at high temperature or for long period of time.

[0037] FIG 1c illustrates that to control the flow deformation using method 1 of the present invention ~~in effect~~ creates a non-smoothed surface.

[0038] FIGS. 2a & 2b are diagrams that illustrate the thickness of glass body before and after the crystallization process.

[0039] FIGS. 2c & 2d are diagrams that illustrate the thickness of glass body, before and after crystallization process, which mixes the glass bits with flat glass pieces together.

[0040] FIG. 2e illustrates the method of loading the glass particles with both glass bits and glass pieces.

[0041] FIG. 2f illustrates the result of the crystallized glass panel with an uneven surface

of 2e.

DETAILED DESCRIPTION

[0042] Method 1: ~~The crystallized glass articles are commonly produced with a smoothed surface. The crystallizing process requires the glass body to be at a temperature where the flow deformation is advanced in order for the surface to be totally smoothed out. It is suggested in the previous patents (ref. Patents G.B. 1427792, U.S. Pat. No. 3,843,343, U.S. Pat. No. 3,955,989, U.S. Pat. No. 4,054,435) that to keep the glass body at about 1150.degree. C. for one hour to complete the crystallizing and flow deformation processes. It is our~~ The present invention to control the flow deformation process, so the spaces among glass particles are filled with glass flow, but the glass particles are not completely flattened down. To do so, we divide the procedure into two steps as follows:

[0043] 1) keep the glass body at a temperature lower than the temperature that the flow deformation process needs (about ~~20.degree.~~ 20° C. below liquidus temperature) for a period of time, then

[0044] 2) raise up the temperature to where the flow deformation process requires for time as needed.

[0045] The first step of process provides enough time for the crystals to grow within the glass body. It also prepares the glass body in temperature close to the flow deformation process needs, so the flow can happen quickly as soon as the temperature rises. In step two, we control the time factor of the process to obtain the desired surface condition as we needed. It is important to know that the formula of glass, the size of the glass particles, the type of furnace used, and the required deviation in depth over the surface are all important factors in determining those temperature and time parameters. The basic procedure is as follows:

[0046] 1. To prepare crystallizable glass bits with size of 10 mm or less such as by water

granulation.

[0047] 2. Apply mold release agent, such as alumina powder, over the refractory mold and frames to prevent the glass from adhering on the mold during the crystallization.

[0048] 3. Putting the glass bits ~~in 1)~~ created in step 1 into the mold over the mold release agent and leveling the surface.

[0049] 4. Place the mold into furnace for crystallization heat-treatment.

[0050] 5. ~~In conjunction with the crystallizing process, kept the glass body at about 20.degree. C. below the temperature of flow deformation process~~ Maintain the glass body about 20° C. below the liquidus temperature for ~~a period of time~~ approximately 40 minutes, so the crystals are formed inside the glass bits and the glass bits are all fusion-bonded together

[0051] 6. Kept the glass body at the temperature where the flow deformation process requires for a period of time ~~as desired~~ such that spaces among glass particles are filled with glass flow, but the glass particles are not completely flattened down.

[0052] 7. Polishing the surface ~~as desired and~~ to remove sharp bumps such that a textured surface with craters with a depth of 0.2 to 0.5 mm is produced.

[0053] Method 2: The thickness of the crystallized glass article is usually about 40% 60% (depends upon the size of particles) of the height of the glass body before it is crystallized, This is due to the fact that different size of glass particles, after fusion bonded together, produces different porous body, and therefore results different density of the article (ref U.S. Pat. No. 4,054,435). On the other hand, the density of the glass body varies the thickness of the glass article. It is our invention to load the glass body with different glass particles, so it has different density in different locations among the glass body. Controlling the time of flow deformation process can produce crystallized

glass panel with un-even surface. The basic procedure is as follows:

[0054] 1. To prepare crystallizable glass bits with size of 5 mm or less such as by water granulation.

[0055] 2. To prepare flat ~~crystallizable/~~ crystallized glass pieces with thickness and shapes desired (circle, square, ~~hex, etc . . .~~).

[0056] 3. Apply mold release agent over the refractory mold and frames to prevent the glass from adhering on the mold during the crystallization.

[0057] 4. Place the flat crystallized glass pieces prepared in ~~2)~~ step 2 on the mold over the mold release agent in position desired.

[0058] 5. Fill up the mold with glass bits prepared in ~~1)~~ step 1. The glass bits ~~may/may not~~ typically cover the surface of the flat crystallized glass pieces.

[0059] 6. Place the mold into furnace for crystallization heat-treatment.

[0060] 7. ~~In conjunction with the crystallizing process, kept the glass body at about 20.degree. C. below the temperature of flow deformation process~~ Maintain the glass body about 20° C. below the liquidus temperature for ~~a period of time~~ approximately 40 minutes, so the crystals are formed inside the glass bits and the glass bits are all fusion-bonded together

[0061] 8. Kept the glass body at the temperature where the flow deformation process requires for a period of time or ~~as desired~~ such that. spaces among glass particles are filled with glass flow. but the glass particles are not completely flattened down.

[0062] 9. Polishing the surface ~~for desired finishing.~~ such that a textured surface with raised areas up to 1.2 mm in height is produced.

EXAMPLES

[0063] The crystallizable glass bits used ~~is within SiO.sub.2--Al.sub.2O.sub.3--CaO--ZnO.~~ in preparing the examples are compositions of the SiO_2-Al_2O_3-CaO-ZnO system. The size of the mold is around 1000 mm.times.1000 mm. The refractory mold is coated with ~~Al.sub.2O.sub.3~~ alumina to prevent the glass from adhering on the mold during the crystallization.

Example 1

[0064] Two sizes of crystallizable glass bits are used, one with size between 3-5 mm (type A) and another with size 3 mm or less (type B). Load 25 kg glass bits of type B into the mold over the mold release agent and level the surface. Load another 25 kg glass bits of type A into mold over the glass bits previously loaded. Leveling the surface. Place the mold into furnace~~ and follow its regular temperature profile for heat-treatment. Maintain the temperature~~ , bring temperature to 1115.degree. C. and maintain temperature for 40 minutes. The crystals are then formed inside the glass bits and the glass bits are all fusion-bonded together. ~~Maintain~~ Increase the temperature to ~~1135.degree~~. 1135° C. and maintain temperature for 30 minutes. In completion of cooling process, polish the surface as desired. The polished article has craters on surface uniformly with average size >5 mm and depth of 0.2 0.5 mm.

Example 2

[0065] The crystallizable glass bits with size of 3 mm or less and flat crystallized glass pieces with size of 30 mm.times.30 mm and thickness of 3 mm are used. The flat crystallized glass pieces are placed on the mold over the mold release agent with 100 mm apart. Load 50 kg glass bits into the mold over flat glass pieces and level the surface. Place the mold into furnace and follow its regular temperature profile for heat-treatment. Maintain the temperature to 1115.degree. C. for 40 minutes. The crystals are then formed

inside the glass bits and the glass bits are all fusion-bonded together. Maintain the temperature to 1135.degree. C. for 30 minutes. In completion of cooling process, polish the surface as desired. The polished article has square shaped bumps on surface uniformly with average size <30 mm and depth <1.2 mm.

METHODS FOR THE PRODUCTION OF CRYSTALLIZED GLASS PANEL WITH EMBOSSED SURFACE

What is claimed is:

1. (currently amended) A method of producing ~~an embossed~~ a crystallized glass article with textured surface, comprising the steps of: ~~Preparing small size of~~

Providing crystallizable glass bits ~~, each of said bit having a property that when heat-treated at certain temperature, needle-like .beta.-wollastonite crystals are formed, said crystals extending from the surface into the interior of the glass body~~. ;

Packing the ~~said~~ glass bits into a mold to form a layer[[.]] ;

Heat-treating the ~~said glass article,~~ loaded mold at a temperature below the liquidus temperature so all the individual small glass bits are fusion-bonded ~~along . Each of said fusion-bonded small glass bits having needle-like .beta.-wollastonite crystals extending from the surface into the interior of the glass body.~~ And crystallize internally;

Heat-treating the ~~said glass article~~ loaded mold at liquidus temperature, so the ~~liquidated~~ liquefied glass ~~flow on the surface would~~ flows to fill in ~~all spaces~~ voids among ~~fusion-bonded~~ glass bits
~~. Stop the process before the glass bits on the surface are completely flattened down.~~

Interrupting flow deformation before all the individual glass bits have flattened, such that the cooled body will have a top surface with bumps with height greater than 0.5 mm. ~~Polishing the finished glass article to remove sharp bumps and results embossed surface pattern.~~

2. (currently amended) The ~~crystallized glass article claimed in~~ method of claim 1, wherein ~~said glass bits of~~ the provided crystallizable glass bits ~~consist essentially of SiO.sub.2, Al.sub.2O.sub.3, and CaO.~~ are composed of one of the following systems: SiO_2-Al_2O_3-CaO or SiO_2-Al_2O_3-Cao-ZnO.

3. (canceled)

4. (currently amended) The ~~crystallized glass article claimed in~~ method of claim 1, wherein ~~said glass bits of~~ the provided crystallizable glass bits have size of less than 10 mm.

5.(canceled)

6. (currently amended) The ~~crystallized glass article claimed in~~ method of claim 1, ~~wherein said polishing is to remove limited top portion of bumps.~~ further including the step of: polishing the cooled glass article to remove part of the bumps on the top surface,

such that a textured surface having a nominal flat surface and unpolished craters with a depth of 0.2 to 0.5 mm is produced.

7. (currently amended) A method of producing a~~n un-even~~ crystallized glass article with an embedded surface pattern, comprising the steps of:
~~Preparing small size of crystallizable glass bits, each of said bit having a property that when heat-treated at certain temperature, needle-like .beta.-wollastonite crystals are formed, said crystals extending from the surface into the interior of the glass body, and~~
Providing flat ~~crystallizable/~~crystallized glass pieces[[.]] ;

~~Packing the said glass bits and pieces into mold to form a layer by~~ Placing the provided flat glass pieces ~~on~~ in ~~the~~ a mold ~~over the mold release agent then~~ such that the flat pieces are spaced apart and placed flat upon the floor of the mold;

Providing crystallizable glass bits;

~~fill up~~ Packing the mold with the provided glass bits~~. The glass bits may/may not cover the surface of the glass pieces.~~ such that the glass bits form a layer that will shrink upon heat treatment to a fused article approximately as thick as the height of the flat crytallized glass pieces placed on the floor of the mold;

Heat-treating the ~~said glass article,~~ loaded mold at a temperature below the liquidus temperature of the glass bits so all the individual small glass bits ~~and glass pieces being fusion-bonded. Each of said fusion-bonded small glass bits and glass pieces having needle-like .beta.-wollastonite crystals extending from the surface into the interior of the glass body.~~ crystallize internally;

Heat-treating the ~~said glass article~~ loaded mold at liquidus temperature, so the ~~liquidated~~ liquefied glass ~~flow on the surface would~~ flows to fill in ~~all spaces~~ voids among ~~fusion-bonded~~ the glass bits ;
~~. Stop the process before the glass bits on the surface are completely flattened down.~~
~~Polishing the finished glass article for smooth or embossed un-even surface.~~

Interrupting flow deformation before all the individual glass bits have flattened, such that the cooled body will have a top surface with bumps with height greater than 0.5 mm; and

Polishing the glass article such that the upper surfaces of the flat glass pieces are exposed and polished and such that the upper surface of the glass article between the flat glass pieces retains unpolished craters with a depth of at least 0.2 mm.

8. (canceled)
9. (canceled)
10. (canceled)

11. (currently amended)The ~~crystallized glass article claimed in~~ method of claim 7, wherein said ~~glass bits of~~ crystallizable glass bits have ~~size of~~ a largest dimension of less

than 10 mm.

12. (canceled)
13. (canceled)

14. (New) A method of producing a crystallized glass plate with an embedded surface pattern, comprising the steps of:

Providing flat pieces of a suitable material that does not shrink or deform after heat treatment;

Placing the flat pieces in a refractory mold such that the flat pieces are spaced apart and placed flat upon the floor of the mold;

Providing crystallizable glass bits;

Packing the provided crystallizable glass bits into the mold over the flat pieces such that the glass bits form a layer that will shrink upon heat treatment to cover the flat crystallized glass pieces placed on the floor of the mold by at least 0.5 mm;

Heat-treating the loaded mold at a temperature below the liquidus temperature of the crystallizable glass bits such that the individual small glass bits crystallize internally;

Heat-treating the loaded mold at the liquidus temperature of the crystallizable glass bits, such that the liquefied glass flows to fill in voids among glass bits and such that the glass plate will have raised portions on the upper surface over the flat pieces that are at least 1 mm high.

15. (New) The process of claim 14, further including the step of:

Polishing the cooled glass plate such that the surfaces of the raised portions over the flat pieces are polished and coplanar, and such that the upper surface of the glass plate between the flat pieces remains unpolished.

16. (New) The process of claim 14, wherein the provided flat pieces are flat pieces of crystallized glass, each piece having a decorative outline in top view.

METHODS FOR THE PRODUCTION OF ~~MARBLE-LIKE~~ CRYSTALLIZED GLASS PANEL WITH EMBOSSED SURFACE

ABSTRACT

~~Methods of producing crystallized glass panel (or the same) having an embossed surface to a regular or irregular pattern, thereby producing a stereoscopic aspect and a less slippery surface. In a crystallized glass article consisting of crystallized glass particles (bits or pieces) fusion bonded together, the thickness of the article can be determined by the density of glass particles packed in the mold. Therefore, by preparing different sizes of glass particles in the mold in different areas can produce glass article with various thickness and result un-even surface. Moreover, in controlling the process of flow deformation can produce glass article with embosses surface. The glass particles can be~~ $\cancel{SiO_2\text{-}Al_2O_3\text{-}CaO}$~~,~~ $\cancel{SiO_2\text{-}Al_2O_3\text{-}CaO\text{-}ZnO}$~~, or any other crystallizable glass.~~

Two related methods for producing crystallized glass panels with intrinsically textured top surface. First method uses controlled time and temperature of heat treatment to limit flow deformation such that particles of crystallizable glass do not flatten completely. Optional polishing creates a flat uppermost surface with an embossed texture of unpolished craters. Second method further includes embedded flat pieces of precrystallized glass that result in raised areas on the surface of the finished panel. Top surface of panel has less reflectivity and greater slip resistance compared to conventional fully polished panels.